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Synthesis and characterization of a zwitterionic hydrogel blend with low coefficient of friction

Allen O. Osaheni [a,b], Eric B. Finkelstein [a,c], Patrick T. Mather [a,c], Michelle M. Blum [a,b,*]

[a] Syracuse Biomaterials Institute, Syracuse University, Syracuse, NY 13244, USA
[b] Department of Mechanical & Aerospace Engineering, Syracuse University, Syracuse, NY 13244, USA
[c] Department of Biomedical & Chemical Engineering, Syracuse University, Syracuse, NY 13244, USA

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ABSTRACT

Hydrogels display a great deal of potential for a wide variety of biomedical applications. Often times the performance of these biomimetic materials is limited due to inferior friction and wear properties. This manuscript presents a method inspired by the tribological phenomena observed in nature for enhancing the lubricious properties of poly(vinyl alcohol) (PVA) hydrogels. This was achieved by blending PVA with various amounts of zwitterionic polymer, poly([2-(methacryloyloxy) ethyl] dimethyl-(3-sulfopropyl) ammonium hydroxide) (pMEDSAH). Our results indicate that pMEDSAH acts as an effective boundary lubricant, allowing for reduction in coefficient of friction by more than 80%. This reduction in friction coefficient was achieved while maintaining comparable mechanical and physical properties to that of the neat material. Also, these zwitterionic blends were found to be cytocompatible. Analysis of the structure to property relationships within this system indicate that the zwitterionic polymer served as a boundary lubricant and promoted a reduction in friction through hydration lubrication. This novel approach provides a promising platform for further investigations enhancing the tribological properties of hydrogels for biomedical applications.

Statement of Significance

The novelty of this work stems from showing that zwitterionic polymers can be used as an extremely effective hydrogel boundary lubricant. This work will have significant scientific impact because to date, design of hydrogels has emphasized replication of mechanical properties, but in order for these types of materials to be fully utilized as biomaterials it is imperative that they possess improved tribological and lubrication properties, because ignoring the surface and boundary lubrication mechanism, make these potential load-bearing substitutes incompatible with other natural articulating surfaces, leading the constructs to wear, fail, and damage healthy tissue. Our work also provides unique insight to the structure-property-function relationships of these biomaterials which will be of great interest to the readership of the journal.

1. Introduction

Whenever two surfaces are in normal contact and there is relative tangential motion between them, there is potential for deterioration of one or both of the surfaces. Gradual wear, or the removal of surface material, is typically an undesirable event. Therefore, the need for lubrication arises to minimize the amount of shear stress that develops between opposing surfaces. This reduction in shear stress is characterized by the coefficient of friction (COF).

A number of biological surfaces display fascinating tribological properties. For example, articular cartilage can withstand pressures as high as 3–18 MPa, with sliding velocities rarely greater than a few centimeters per second while maintaining a COF in the range of 0.001–0.03 [1]. Another example is high molecular weight glycosylated glycoproteins found on the surfaces of organs and non-load-bearing tissues which have been shown to play a crucial role in the tribology of the tissues by providing smooth

* Corresponding author at: 239 Link Hall, Mechanical and Aerospace Department, Syracuse University, Syracuse, NY 13244, USA.
E-mail address: mmblum@syr.edu (M.M. Blum).

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lubrication. These include certain mucins for providing lubrication in saliva [2], as well as lubricative coating on the surfaces of cells lining the respiratory, digestive, gastrointestinal and urogenital tracts [3]. Also, Proteoglycan 4 (i.e. Lubricin) in synovial fluid dissipates strain energy induced during motion [4].

Inspired by the tribological phenomena observed in nature, biomaterials engineering strives to create advanced materials whose properties replicate the impressive friction and wear performance that is exhibited by the body. One class of materials showing great promise for biomedical applications is hydrogels, a class of biomimetic polymers that swell in the presence of fluids, yet are insoluble due to their cross-linked structure [5]. Hydrogels, have long been recognized to have potential for biomedical applications due to their mechanical resilience coupled with high water content, analogous to some natural tissues [6–8].

Hydrogels are attractive as a biomedical technology primarily for two reasons: (1) they form a structure that is viscoelastic and permeable so their mechanical properties mimic many of the natural tissues in our body and (2) their tunable structure offers the potential to be easily modified to meet the needs of the desired application. Despite their well-established biocompatibility, inherent biomimetic properties and adaptability, inferior friction and wear properties limit the use of hydrogels in tribologically demanding biomedical applications [9–11] and damage to opposing natural tissue.

Considerable work has gone into mechanical strengthening of hydrogels [12], while other research has focused on understanding and optimizing various fluid film lubrication mechanisms [13,14]. This research focuses on enhancing hydrogel boundary lubrication. In the boundary lubrication regime, the contacting normal surface loads are not supported by the lubricating fluid resulting in a significant amount of solid surface contact. Instead, the pressure is supported by a nanometer scale surface film, also known as a boundary lubricant [15]. In many ways boundary lubrication is the regime which dictates the service life of the contact pair and can be considered the worst case scenario in terms of device performance. In order to enhance hydrogel performance within the boundary lubrication regime, a novel material design was developed by blending a synthetic hydrogel with a zwitterionic polymer, intended to act as a boundary lubricant.

Zwitterionic molecules are net-neutral, yet possess both positive and negative charges in close proximity to each other often along a carbon chain backbone [16]. This unique composition allows these overall neutral molecules to interact with water through strong electrostatic attractions [17]. These systems have been investigated for such applications as protein-resistant anti-fouling substrates [18,19] and coatings [20,21], biocompatible surfaces [22,23] and hydrogel implants [24–27], controlling flow in microfluidic devices [28] and electrostatic ion chromatography [29]. Recently, zwitterionic polymers have been shown to have exceptional performance in boundary lubrication. This behavior is credited to the formation of hydration shells surrounding the charged components of zwitterionic chains promoting a mechanism known as hydration lubrication, supporting loads upwards of 100 MPa [30].

This concept, with basis in prior research [31–34], led to the hypothesis that preparation of zwitterionic hydrogel blends would result in a significant reduction in COF compared to the neat hydrogel material. The primary objectives of this study are to present the synthesis and chemical characterization of the zwitterionic boundary lubricant enhanced hydrogels and also investigate how this approach influences the mechanical, tribological, physical and cytotoxic properties of the resulting hydrogel.

2. Materials and methods

2.1. Materials

Polyvinyl alcohol (PVA, 99% hydrolyzed) with a reported average molecular weight of 130,000 g/mol was purchased from Sigma-Aldrich (St. Louis, MO). The monomer ([2-(methacryloyloxy) ethyl] dimethyl-(3-sulfopropyl) ammonium hydroxide) (MEDSAH), solvent N, N-dimethylformamide (DMF) and initiator 2,2′-azobisisobutyronitrile (AIBN) were also obtained from Sigma-Aldrich. All chemicals were used as received.

2.2. Sample fabrication

2.2.1. PVA hydrogel (PVA-H) fabrication

Neat PVA-H was prepared following a prior report with modifications [40]. Solutions were first prepared by solvent casting a 40 wt% (m/v) mixture of PVA and deionized (DI) water. The mixture was heated at 90 °C in an isothermal oven (Fisher Scientific, Waltham, MA) for 6 h resulting in a viscous, transparent solution. Stirring was not done during solvent casting due to the high viscosity of the solution and propensity to bubble formation. Following solvent casting, samples were subjected to four freeze-thaw cycles where samples were frozen at −80 °C for 30 min and then allowed to thaw at room temperature for 30 min. This cyclic freeze-thaw process is understood to reinforce the hydrogel structure through formation of crystalline regions, the concentration of these crystalline regions increasing with each successive freeze-thaw cycle [7]. Following the freeze thaw process, samples were submerged in DI water for at least 48 h to ensure they reached equilibrium swelling.

2.2.2. Polymerization of MEDSAH

The zwitterionic polymer poly(MEDSAH) (hereafter pMEDSAH) was prepared through the free radical polymerization of MEDSAH initiated by AIBN under nitrogen in a 60:40 vol ratio of DMF:DI water solution containing 6.7 wt% MEDSAH and a 100:1 monomer to initiator mass ratio (58.78:1 mol ratio) (Fig. 1). The reaction was performed at 65 °C for 6 h at which point the precipitated product was harvested.

2.2.3. Hydrogel blend fabrication

The hydrogel blends were fabricated by initially preparing a 40 wt% (m/v) mixture of PVA to DI water with pMEDSAH contents ranging from 1 to 30 wt% relative to PVA. pMEDSAH was dissolved in DI water via the assistance of a Vortex-Genie 2 mixer (Scientific Industries Inc., Bohemia, NY). The mixtures were heated at 90 °C for 6 h resulting in a viscous solution. Each solution was then subjected to four freeze-thaw cycles where samples were frozen

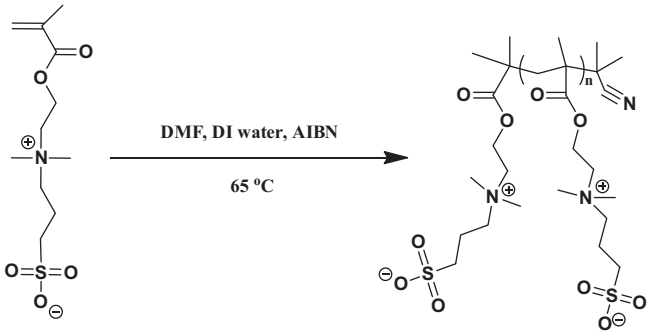

Fig. 1. Schematic depicting the polymerization of MEDSAH.